STUDY OF THE EFFECT OF FUNCTIONALIZATION OF CARBON NANOTUBES ON GAS SEPARATION

M. Babaei[1], M. Anbia[2*] and M. Kazemipour[1]

[1] Islamic Azad University, Department of Chemistry, Kerman, Iran. ORCID: 0000-0002-0615-118X; ORCID: 0000-0002-8485-3291
[2] Iran University of Science and Technology, Faculty of Chemistry, Research Laboratory of Nanoporous Materials, Tehran, Iran.
E-mail: anbia@iust.ac.ir - ORCID: 0000-0002-2142-3219

Abstract - In order to improve the adsorption capacity and selectivity of CO_2/CH_4 and CO_2/N_2, we have functionalized multi-walled carbon nanotubes (MWCNT) with 3-aminopropyltriethoxysilane (APTES). The functionalized MWCNT was characterized by Fourier transform infrared (FT-IR), energy dispersive X-ray spectroscopy (EDX) and BET analysis. CO_2, CH_4 and N_2 adsorption at two different temperatures and P < 5 bar on the functionalized MWCNTs was investigated by the volumetric method. The selectivity of the functionalized MWCNTs for CO_2/CH_4 and CO_2/N_2 was studied and compared with MWCNTs. The functionalized MWCNTs show higher adsorption capacity of CO_2 and selectivity of CO_2/CH_4 and CO_2/N_2 in comparison with the MWCNTs at different pressures. The highest CO_2/CH_4 and CO_2/N_2 selectivities for the functionalized MWCNTs were 6.78 and 26.14, respectively, at a pressure of 0.2 bar and at 298 K. Two of the most common adsorption models, the Langmuir and Sips isotherms, were used to correlate the experimental data of CO_2 and CH_4 adsorption on the adsorbents. The results confirm that the functionalized MWCNTs are promising materials for the separation and purification of gases.
Keywords: Carbon nanotubes; Functionalization; Adsorption isotherm; Gas separation.

INTRODUCTION

The continuous use of fossil fuels has led to emission of greenhouse gases and global warming, which is one of the most important environmental issues facing human beings. Two ways can decrease the emission of CO_2: (1) carbon capture and storage (CCS) and (2) use of clean and renewable energy sources. An ideal replacement for fossil fuels is natural gas because it releases less greenhouse gases (Chong et al., 2016; Lajunen et al., 2016). Natural gas is mainly composed of methane, but contains impurities such as CO_2, H_2S and H_2O, which decrease the energy content and corrode pipelines (Campo et al., 2016; Faramawy et al., 2018; Kajama et al., 2018). Therefore, removing these components from natural gas is important in its industrial application. In order to separate the gas mixtures into their component parts, a variety of methods have been proposed such as solvent absorption, membrane separation, adsorptive separation, and chemical conversion. Among the gas separation methods, adsorptive separation appears to be important for gas separation/purification and storage technology owing to its simplicity, low cost, ease of control, and high energy performance (Peng et al., 2006; Babarao et al., 2009; Li et al., 2009).

A lot of porous materials, such as zeolites (Cavenati et al., 2004; Su et al., 2010), activated alumina (Luebke et al., 2006; Carreon et al., 2008), metal organic frameworks (MOFs) (Belmabkhout et al., 2009; Xiang et al., 2010) and carbonaceous materials (Przepiórski et al., 2004; Lu et al., 2008; Budaeva et al., 2010; Palmer et al., 2011; Lei et al., 2014) have been utilized in gas adsorption/separation processes. Recently, there is a lot of interest in utilizing CNTs for CO_2 adsorption due to their distinctive chemical and physical properties, high thermal and chemical stability and also the reversible nature of the CO_2 adsorption process upon increasing

* Corresponding author: M. Anbia - E-mail: anbia@iust.ac.ir

the temperature (Su et al., 2009; Shen et al., 2010; Khoerunnisa et al., 2014; Wang et al., 2016).

Investigation of the effect of surface functional groups on the textural properties of carbonaceous materials such as surface area and pore size distribution and also on the adsorption/separation of gases has shown that modification of the surface of carbonaceous materials could cause selective adsorption of one molecule over another (Bezerra et al., 2011; Su et al., 2011; Hu et al., 2017; Keller et al., 2018). The functionalization of CNTs can be performed with a wide range of functional groups including oxygen- and nitrogen-containing groups. Incorporation of nitrogen-containing groups enhances the basicity of CNTs and thus can improve capacity and selectivity of carbonaceous materials in adsorption of acidic gases such as CO_2 and SO_2 (Fatemi et al., 2011; Gui et al., 2013; Khalili et al., 2013; Irani et al., 2017; Zhou et al., 2017).

A large number of experimental studies on single gas adsorption in carbon nanotubes have been reported in literature, but experimental studies on the gas compounds and separation of their mixtures, especially on CNTs, are seldom found. Therefore, further studies are needed to improve the performance of CNTs for gas separation. In this work, a kind of multiwall carbon nanotubes (MWCNT) is functionalized by 3-aminopropyltriethoxysilane (APTES) and its application for CO_2 separation studied. The adsorption isotherms for pure components are obtained at two temperatures. The adsorption capacity and selectivity of the MWCNTs are investigated at 298 K and 348 K.

EXPERIMENTAL SECTION

Materials

Commercial MWCNTs (Neutrino Corporation) with inner diameter 5-10 nm and 95% purity were used in this study. Nitric acid 65% (HNO_3), sulfuric acid 95–97% (H_2SO_4) and APTES were obtained from E. Merck (Germany). The solvent used in this work was ethanol obtained from Merck. The CO_2, CH_4 and N_2 gas cylinders with purity > 99.999 used in adsorption experiments, were supplied by Sepehr Gas Kavian Co.

Preparation of adsorbent

Acid pre-treatment of MWCNTs was performed to achieve two aims: (1) removal of metal catalyst particles from the pristine MWCNTs and (2) carboxylation of the MWCNTs to introduce carboxyl groups on the MWCNT surface prior to amine functionalization. The oxidized MWCNT (MWCNT-COOH) was prepared by adding 500 mg of the calcined MWCNTs to 80 mL of a mixture of H_2SO_4/HNO_3 (3:1 v/v) via sonication for 1 h. Then the solution was stirred with a magnetic stirrer, at room temperature for 24 h. The mixture was diluted with distilled water and filtered through a 0.2 µm fiber filter and washed with distilled water several

times until the pH increased to neutral (pH 7). The carboxylated MWCNT were then dried in a vacuum drying oven at 100 °C for 4 h (Anbia et al., 2012).

The amine functionalization was then carried out on the pretreated MWCNTs using APTES. The pre-treated MWCNTs were dispersed into bottles containing APTES solution (10 mL of 97% APTS + 90 mL of ethanol) and continuously stirred with a magnetic stirrer at room temperature for 72 h. The mixture was filtered through a 0.2 µm fiber filter and washed repeatedly with ethanol and deionized water to remove excess APTES. Finally the filtered solid was dried in an oven at 100 °C for 6 h and denoted as N-MWCNT.

Characterization

The surface functional groups of the modified sorbents were evaluated by FTIR spectra obtained with a FT-IR DIGILAB FTS 7000 spectrometer. The chemical composition of N-MWCNT was studied by energy dispersive X-ray spectroscopy (EDX). The specific surface area and the pore diameter of the adsorbents were obtained by N_2 adsorption–desorption isotherms at 77 K with a volumetric sorption analyzer.

Gas adsorption measurement

To evaluate the CO_2, CH_4 and N_2 adsorption capacity of adsorbents at two different temperatures, a laboratory setup based on the volumetric method was used, which is schematically shown in Fig. 1. At first, 0.5 g of adsorbent was poured into the adsorption reactor and then attached to the system. To ensure that there is no leak in the connections, the system was checked with the inert Helium gas flow. In order to degas the system, the valves 6, 7, 8, 9 were opened and other valves closed; then, the system was evacuated with the vacuum pump for 1.5 h at 120ºC. After degassing the adsorption system, temperature was decreased to ambient temperature. To perform the adsorption test, we opened the valves 1, 3, 5, 6, 7 and 8 while other valves were closed. The pressure drop observed during the process was the result of gas adsorption and some dead volumes in the reactor. We could exactly measure
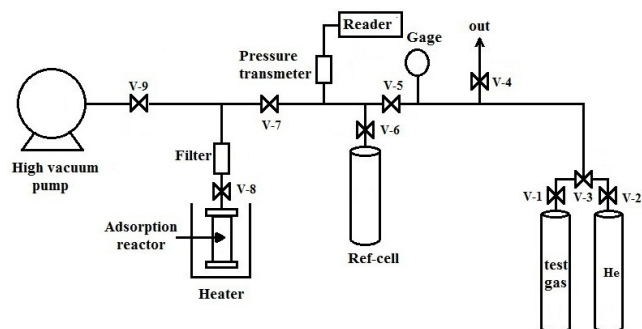

Figure 1. Schematic of volumetric system for adsorption test.

pressure reduction relevant to the gas adsorption by measuring the dead volumes via helium test. The CO_2, CH_4 and N_2 used for the experiment were of 99.99 % purity (Jin et al., 2015; Li et al., 2016; Jin et al. 2018).

RESULT AND DISCUSSION

Adsorbents characterization

Fig. 2 shows the FTIR spectra of calcined and amine modified MWCNTs. In the calcined MWCNT spectrum, the peak at 1630 cm^{-1} is attributed to C=C bonds of nanotubes. The peak at 3432 cm^{-1} is associated with hydroxyl groups (−OH) on the surface of the adsorbents. The IR spectrum of N-MWCNT shows significant bands at 3439, 2850-2960, 1743, 1355-1488, 1030-1100 and 803 cm^{-1} which are associated with CH stretching from $CH_2CH_2CH_2-NH_2$ groups, N-H stretch, N-H_2 deformation of hydrogen-bonded amine group (Chang et al., 2003; Huang et al., 2003), Si-O-Si(C) and O-Si-O vibrations (Jing et al., 2002; Zhang et al., 2005), respectively. The presence of these peaks confirms the incorporation of APTES on the surface of MWCNTs.

In order to confirm the incorporation of APTES on the surface of MWCNTs, an EDX experiment was performed with a LN (Liquid Nitrogen) free Energy Dispersive detector (SAMx SDD detector) attached to a SEM (Philips XL-30). The results of EDX elemental microanalysis of the N-MWCNT are listed in Table 1.

Figs. 3 and 4 show the N_2 adsorption/desorption isotherms and the BJH pore size distribution of MWCNT and N-MWCNT. It is seen that the modified MWCNTs have less adsorption capacity of N_2, because a smaller amount of porosity is retained after the incorporation of APTES on the modified MWCNT surface. The textural properties of the adsorbents are given in Table 1. It is seen that the surface area has decreased but the average pore diameter has increased. The decrease of the surface area could be explained by the blockage of pore entrances due to the formation of the amine groups on the surface of N-MWCNT and
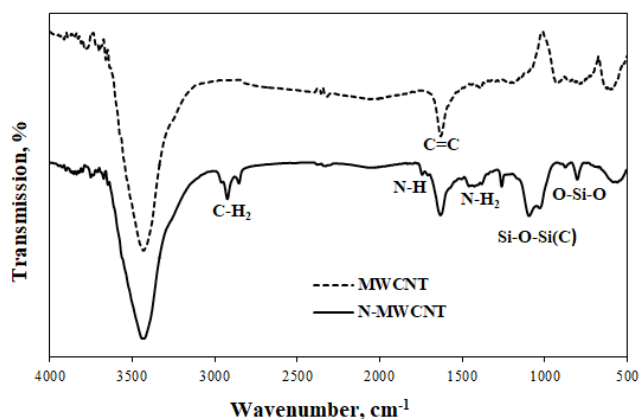

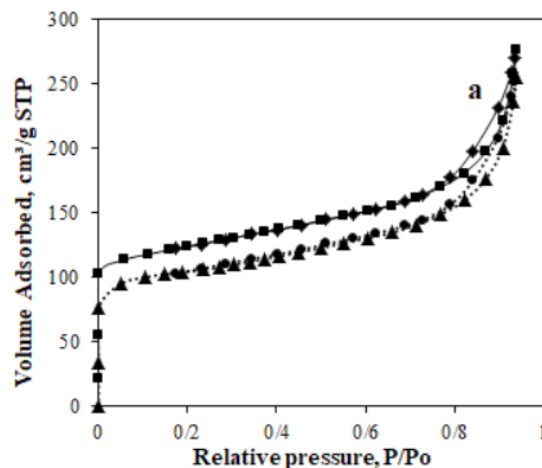**Figure 2.** FT-IR spectra of MWCNT and N-MWCNT.

Figure 3. N_2 adsorption-desorption isotherms of a) MWCNT and b) N-MWCNT at 77 K.
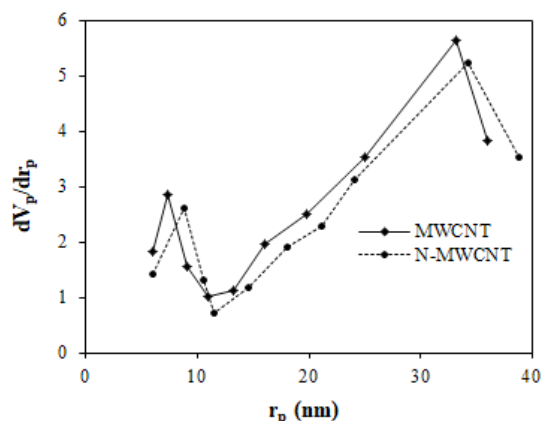

Figure 4. BJH pore size distribution of MWCNT and N-MWCNT.

Table 1. Textural properties and EDX analysis of the MWCNT and N-MWCNT (elemental composition (atomic %)).

Adsorbate	MWCNT	N-MWCNT
S_{BET} (m^{2}g^{-1})	>200	137
Mean pore diameter (nm)	7.4	8.6
C	-	78.65
N	-	4.24
O	-	10.94
Si	-	6.16

the increase of the average pore diameter is due to the removal of the amorphous carbon and the catalysts during the purification process by acidic solution (Ioannatos et al., 2010; Su et al., 2009).

Adsorption measurement

Fig. 5 shows the pure CO_2, CH_4 and N_2 adsorption isotherms on MWCNT and N-MWCNT at 298 K. The CO_2, CH_4 and N_2 adsorption capacities of MWCNT and N-MWCNT at 298 K and 348 K and P = 1 bar are given in Table 2.

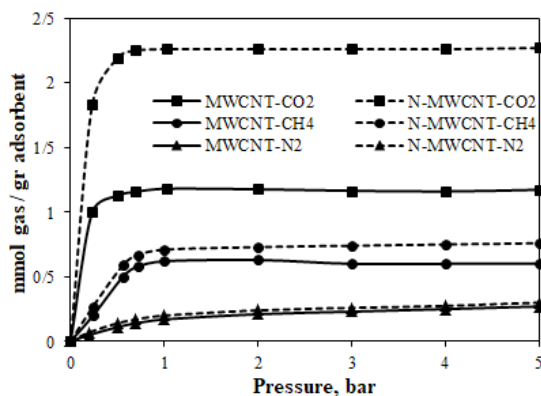As expected, adsorption capacity of the three gases was enhanced after amine modification of MWCNTs.

Figure 5. Adsorption isotherms of CO_2, CH_4 and N_2 on MWCNT and N-MWCNT at 298 K.

Table 2. Gas adsorption capacities of MWCNT and N-MWCNT at two temperatures and 1 bar.

Adsorbent	Gas adsorption capacity (mmol/g)					
	298 K			348 K		
	CO_2	CH_4	N_2	CO_2	CH_4	N_2
MWCNT	1.19	0.63	0.17	1.02	—	0.09
N-MWCNT	2.26	0.71	0.2	1.99	—	0.17

However, as seen in Fig. 5, the N-MWCNT presents a significant increase in the adsorption capacity of CO_2 in comparison with CH_4 and N_2 which may be due to the reaction between the surface amine groups with the CO_2 molecules and also because of the high quadrupole moment of CO_2 molecules. Chemical reactions between amine groups and CO_2 produce the carbamate species according to Eq. (1):

$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^- \qquad (1)$$

$$RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO_3^- \qquad (2)$$
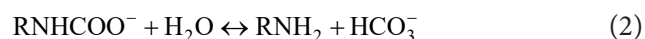
However, as seen in Table 2, the CO_2 and N_2 adsorption capacity decreases with increasing temperature. The decrease of adsorption capacity with rising temperature implies that the adsorption process is exothermic.

Two of the most common adsorption models, the Langmuir (Garnier et al., 2011) and Sips (Foo et al., 2010) isotherms, were used to correlate the experimental data of CO_2 and CH_4 adsorption on MWCNT and N-MWCNT at 298 K. The values of model parameters are given in Table 3. The Langmuir isotherm corresponds to homogeneous adsorbent surfaces (Purna Chandra Rao et al., 2006). The Langmuir isotherm is represented by the following equation:

$$q = q_m \frac{bP}{(1+bP)} \qquad (3)$$

where q is the adsorbed capacity (mmol g^{-1}) at equilibrium pressure P, q_m (mmol g^{-1}) and b (KPa^{-1}) are the maximum amount of gas adsorbed (mmol g^{-1}) and the Langmuir constant, respectively.

The Sips isotherm is the combined formula of the Langmuir and Freundlich equations, which is given by Eq.(4):

$$q = q_m \frac{(bP)^{1/n}}{1+(bP)^{1/n}} \qquad (4)$$

where q (mmol g^{-1}) is the amount of gas adsorbed at equilibrium pressure of P (KPa), q_m (mmol g^{-1}) is the maximum adsorption capacity, b (KPa^{-1}) is the adsorption equilibrium constant which shows the adsorbate affinity for the surface of adsorbent, and n is the heterogeneity parameter (Do, 1998).

The fitting accuracy of the proposed model for the experimental data was estimated by an error function based on the average percent deviation calculated according to:

$$ARE\% = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_i^{exp} - q_i^{cal}}{q_i^{exp}} \right| \qquad (5)$$

where ARE (%) is the average percent deviation, N is the number of data points available in the adsorption equilibrium isotherms, and q^{exp} and q^{cal} are the experimental and calculated amounts adsorbed (mmol/g), respectively.

As shown in Table 3, between the two isotherms mentioned above, the Sips isotherm with high correlation coefficients ($R^2 > 0.99$) and an average percent deviation value of less than 3% provides the best model for adsorbents, and presents the excellent agreement between the model parameters and the experimental data, which indicates the heterogeneous nature of the adsorbent surface.

Comparisons of the CO_2 adsorption capacities of the adsorbents used in this study and other porous materials are given in Table 4.

Table 3. Langmuir and Sips isotherm parameters for the adsorption of gases on adsorbents at 298K.

Adsorbent	CO_2		CH_4	
	MWCNT	N-MWCNT	MWCNT	N-MWCNT
Sips				
q_m (mmol/g)	1.195	2.30	0.614	0.731
b (KPa^{-1})	108.2	231.9	3.22	3.239
n	3.45	4.30	0.34	0.430
R^2	0.991	0.995	0.994	0.999
ARE%	0.595	1.76	2.53	2.95
Langmuir				
q_m (mmol/g)	1.36	2.33	0.671	0.779
b (KPa^{-1})	25.68	19.63	3.56	3.87
R^2	0.997	0.986	0.914	0.957
ARE%	4.71	3.09	6.5	9.71

Table 4. Comparison of the CO_2 adsorption capacity of the MWCNT and N-MWCNT with other porous materials.

Adsorbent	CO_2 adsorption capacity (mg/g)	Conditions	Reference
MCM-48-PEHA-DEA	22.44	298 K	Anbia et al. (2012)
Plasma functionalized CNT	12.6	308 K	Babu et al. (2013)
MWCNT-APTES	25.0	298 K	Lu et al. (2008)
MWCNT-APTES	40.0	323 K	Su et al. (2011)
MWCNT–NH2.	88.0	298 K	Ghaznavi et al. (2012)
MWCNT-APTES	75.4	333 K	Gui et al. (2013)
MWCNT	52.36	298 K	This study
N-MWCNT	99.44	298 K	This study
N-MWCNT	87.56	348 K	This study

Adsorption selectivity for gases

The pure component selectivity for gases was obtained from their adsorption isotherms. By applying Eq. (6) (Pawar et al., 2009), the adsorption selectivity of gas 1 over gas 2 can be calculated, where V_1 and V_2 are the volumes of gases 1 and 2 adsorbed at a certain temperature and pressure, respectively.

$$A_{1/2} = \frac{V_1}{V_{2 \cdot T,P}} \tag{6}$$

The adsorption selectivities of CO_2/CH_4 on MWCNT and N-MWCNT at 1 bar pressure and 298 K are 1.9 and 3.18, respectively. As is clear, the N-MWCNT has higher selectivity to CO_2 than MWCNT. This is due to the increase of the cationic surface of carbon nanotubes which is produced by amine groups and also because of the high quadrupole moment of CO_2 molecules.
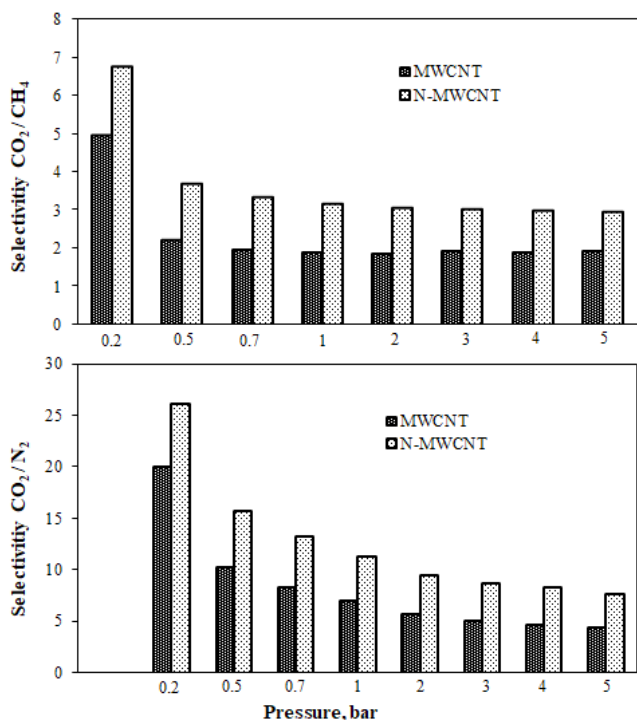
Fig. 6 shows the adsorption selectivities of CO_2/CH_4 and CO_2/N_2 on MWCNT and N-MWCNT at different pressures and 298 K. The CO_2/CH_4 selectivity decreases with increasing pressure. At high pressures, the adsorption of CH_4 becomes more significant than that of CO_2. The smaller and flat molecules of CO_2 can easily diffuse through the pore mouths of nanotubes at lower pressures, whereas large molecules of CH_4 require higher pressure to enter the pores (Fatemi et al., 2011).

The selectivity of CO_2/N_2 on N-MWCNT is higher than on MWCNT. According to the quadrupole moment of CO_2 and N_2 molecules as well as the size of the molecules, this is justified. These results suggest that N-MWCNT is a promising candidate for separation and purification of CO_2 from various gas mixtures by an adsorptive process.

CONCLUSION

The gas adsorption capacities on the functionalized MWCNT have been studied. The adsorption capacity of CO_2, CH_4 and N_2 is enhanced after amine modification of MWCNTs. However, the N-MWCNT presents a significant increase in the adsorption capacity of CO_2 in comparison with CH_4 and N_2. The CO_2/CH_4 and CO_2/N_2 selectivities were improved for N-MWCNT at 298 K. Selectivity of N-MWCNT for a CO_2/CH_4 mixture (6.78) at 298 K and p = 0.2 bar was higher than that of MWCNT (4.99), because CO_2 molecules have high quadrupole moment while CH_4 molecules do not have a quadrupole moment. Selectivities of N-MWCNT and MWCNT for the CO_2/N_2 mixture at p = 0.2 bar and 298 K were 26.14 and 19.96, respectively. It is concluded that N-MWCNT is a promising material for CO_2 capture from gas mixtures.

Figure 6. Selectivities of CO_2/CH_4 and CO_2/N_2 on MWCNT and N-MWCNT at 298 K.

REFERENCES

Anbia, M., Hoseini, V. Development of MWCNT@ MIL-101 hybrid composite with enhanced adsorption capacity for carbon dioxide. Chemical Engineering Journal, 191, 326-330 (2012). https://doi.org/10.1016/j.cej.2012.03.025

Anbia, M., Hoseini, V., Mandegarzad, S. Synthesis and characterization of nanocomposite MCM-48-PEHA-DEA and its application as CO_2 adsorbent. Korean Journal of Chemical Engineering, 29, 1776-1781 (2012). https://doi.org/10.1007/s11814-012-0090-4

Babarao, R., Jiang, J. Unprecedentedly high selective adsorption of gas mixtures in rho zeolite-like metal- organic framework: a molecular simulation study. Journal of the American Chemical Society, 131, 11417-11425 (2009). https://doi.org/10.1021/ja901061j

Babu, D. J., Lange, M., Cherkashinin, G., Issanin, A., Staudt, R., Schneider, J. J. Gas adsorption studies of CO_2 and N_2 in spatially aligned double-walled carbon nanotube arrays. Carbon, 61, 616-623 (2013). https://doi.org/10.1016/j.carbon.2013.05.045

Belmabkhout, Y., Serna-Guerrero, R., Sayari, A. Adsorption of CO_2-containing gas mixtures over amine-bearing pore-expanded MCM-41 silica: application for gas purification. Industrial & Engineering Chemistry Research, 49, 359-365 (2009). https://doi.org/10.1021/ie900837t

Bezerra, D. P., Oliveira, R. S., Vieira, R. S., Cavalcante, C. L., Azevedo, D. C. S. Adsorption of CO_2 on nitrogen-enriched activated carbon and zeolite 13X. Adsorption, 17, 235-246 (2011). https://doi.org/10.1007/s10450-011-9320-z

Budaeva, A. D., Zoltoev, E. V. Porous structure and sorption properties of nitrogen-containing activated carbon. Fuel, 89, 2623-2627 (2010). https://doi.org/10.1016/j.fuel.2010.04.016

Campo, M. C., Ribeiro, A. M., Ferreira, A. F., Santos, J. C., Lutz, C., Loureiro, J. M. , Rodrigues, A. E. Carbon dioxide removal for methane upgrade by a VSA process using an improved 13X zeolite. Fuel Processing Technology, 143, 185-194 (2016). https://doi.org/10.1016/j.fuproc.2015.11.024

Carreon, M. A., Li, S., Falconer, J. L., Noble, R. D. Alumina-supported SAPO-34 membranes for CO_2/CH_4 separation. Journal of the American Chemical Society, 130, 5412-5413 (2008). https://doi.org/10.1021/ja801294f

Cavenati, S., Grande, C. A., Rodrigues, A. E. Adsorption equilibrium of methane, carbon dioxide, and nitrogen on zeolite 13X at high pressures. Journal of Chemical & Engineering Data, 49, 1095-1101 (2004). https://doi.org/10.1021/je0498917

Chang, A. C., Chuang, S. S., Gray, M., Soong, Y. In-situ infrared study of CO_2 adsorption on SBA-15 grafted with γ-(aminopropyl) triethoxysilane. Energy & Fuels, 17, 468-473 (2003). https://doi.org/10.1021/ef020176h

Chong, Z. R., Yang, S. H. B., Babu, P., Linga, P., Li, X.-S. Review of natural gas hydrates as an energy resource: Prospects and challenges. Applied Energy, 162, 1633-1652 (2016). https://doi.org/10.1016/j.apenergy.2014.12.061

Do, D. D. Fundamentals of pure component adsorption equilibria, World Scientific, 2, 13-70 (1998).

Faramawy, S., Zaki, T., Sakr, A.-E., Saber, O., Aboul-Gheit, A., Hassan, S. The activity of Mg-Al layered double hydroxides intercalated with nitrogen-containing anions towards the removal of carbon dioxide from natural gas. Journal of Natural Gas Science and Engineering, 54, 72-82 (2018). https://doi.org/10.1016/j.jngse.2018.04.002

Fatemi, S., Vesali-Naseh, M., Cyrus, M., Hashemi, J. Improving CO_2/CH_4 adsorptive selectivity of carbon nanotubes by functionalization with nitrogen-containing groups. Chemical Engineering Research and Design, 89, 1669-1675 (2011). https://doi.org/10.1016/j.cherd.2010.10.002

Foo, K. Y., Hameed, B. H. Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal, 156, 2-10 (2010). https://doi.org/10.1016/j.cej.2009.09.013

Garnier, C., Finqueneisel, G., Zimny, T., Pokryszka, Z., Lafortune, S., Défossez, P. D. C., Gaucher, E. C. Selection of coals of different maturities for CO_2 Storage by modelling of CH_4 and CO_2 adsorption isotherms. International Journal of Coal Geology, 87, 80-86 (2011). https://doi.org/10.1016/j.coal.2011.05.001

Ghaznavi, F., Fatemi, S., Joda, M., CO_2-CH_4 phase equilibria on modified multi-walled carbon nanotubes using Gibbs excess energy models based on vacancy solution theory. The Canadian Journal of Chemical Engineering, 90, 769-776 (2012). https://doi.org/10.1002/cjce.20526

Gui, M. M., Yap, Y. X., Chai, S.-P., Mohamed, A. R. Multi-walled carbon nanotubes modified with (3-aminopropyl)triethoxysilane for effective carbon dioxide adsorption. International Journal of Greenhouse Gas Control, 14, 65-73 (2013). https://doi.org/10.1016/j.ijggc.2013.01.004

Hu, H., Zhang, T., Yuan, S., Tang, S. Functionalization of multi-walled carbon nanotubes with phenylenediamine for enhanced CO_2 adsorption. Adsorption, 23, 73-85 (2017). https://doi.org/10.1007/s10450-016-9820-y

Huang, H. Y., Yang, R. T., Chinn, D., Munson, C. L. Amine-grafted MCM-48 and silica xerogel as superior sorbents for acidic gas removal from

natural gas. Industrial & Engineering Chemistry Research, 42, 2427-2433 (2003). https://doi.org/10.1021/ie020440u

Ioannatos, G. E., Verykios, X. E. H_2 storage on single- and multi-walled carbon nanotubes. International Journal of Hydrogen Energy, 35, 622-628 (2010). https://doi.org/10.1016/j.ijhydene.2009.11.029

Irani, M., Jacobson, A. T., Gasem, K. A., Fan, M. Modified carbon nanotubes/tetraethylenepentamine for CO_2 capture. Fuel, 206, 10-18 (2017). https://doi.org/10.1016/j.fuel.2017.05.087

Jin, K., Zhang, T., Ji, J., Zhang, M., Zhang, Y., Tang, S. Functionalization of MCM-22 by dual acidic ionic liquid and its paraffin absorption modulation properties. Industrial & Engineering Chemistry Research, 54, 164-170 (2015). https://doi.org/10.1021/ie504327t

Jin, K., Zhang, T., Yuan, S., Tang, S. Regulation of isobutane/1-butene adsorption behaviors on the acidic ionic liquids-functionalized MCM-22 zeolite. Chinese Journal of Chemical Engineering, 26, 127-136 (2018). https://doi.org/10.1016/j.cjche.2017.05.023

Jing, S.-Y., Lee, H.-J., Choi, C. K. Chemical bond structure on Si-OC composite films with a low dielectric constant deposited by using inductively coupled plasma chemical vapor deposition. Journal of the Korean Physical Society, 41, 769-773 (2002).

Kajama, M. N., Yildirim, Y., Taura, U. H., Grema, A. S., Abdulrahman, S. Silica Modified Membrane for Carbon Dioxide Separation from Natural Gas. Nano Hybrids and Composites, 21, 43-52 (2018). https://doi.org/10.4028/www.scientific.net/NHC.21.43

Keller, L., Ohs, B., Lenhart, J., Abduly, L., Blanke, P., Wessling, M. High capacity polyethylenimine impregnated microtubes made of carbon nanotubes for CO_2 capture. Carbon, 126, 338-345 (2018). https://doi.org/10.1016/j.carbon.2017.10.023

Khalili, S., Ghoreyshi, A. A., Jahanshahi, M., Pirzadeh, K. Enhancement of Carbon Dioxide Capture by Amine-Functionalized Multi-Walled Carbon Nanotube. Clean-Soil, Air, Water, 41, 939-948 (2013). https://doi.org/10.1002/clen.201200339

Khoerunnisa, F., Minami, D., Fujimori, T., Hong, S., Choi, Y., Sakamoto, H., Endo, M., Kaneko, K. Enhanced CO_2 adsorptivity of SWCNT by polycyclic aromatic hydrocarbon intercalation. Adsorption, 20, 301-309 (2014). https://doi.org/10.1007/s10450-013-9578-4

Lajunen, A., Lipman, T. Lifecycle cost assessment and carbon dioxide emissions of diesel, natural gas, hybrid electric, fuel cell hybrid and electric transit buses. Energy, 106, 329-342 (2016). https://doi.org/10.1016/j.energy.2016.03.075

Lei, G., Liu, C., Xie, H., Song, F. Separation of the hydrogen sulfide and methane mixture by the porous graphene membrane: Effect of the charges. Chemical Physics Letters, 599, 127-132 (2014). https://doi.org/10.1016/j.cplett.2014.03.040

Li, H., Zhang, T., Yuan, S., Tang, S. MCM-36 zeolites tailored with acidic ionic liquid to regulate adsorption properties of isobutane and 1-butene. Chinese Journal of Chemical Engineering, 24, 1703-1711 (2016). https://doi.org/10.1016/j.cjche.2016.05.033

Li, J.-R., Kuppler, R. J., Zhou, H.-C. Selective gas adsorption and separation in metal-organic frameworks. Chemical Society Reviews, 38, 1477-1504 (2009). https://doi.org/10.1039/b802426j

Lu, C., Bai, H., Wu, B., Su, F., Hwang, J. F. Comparative study of CO_2 capture by carbon nanotubes, activated carbons, and zeolites. Energy & Fuels, 22, 3050-3056 (2008). https://doi.org/10.1021/ef8000086

Luebke, D., Myers, C., Pennline, H. Hybrid membranes for selective carbon dioxide separation from fuel gas. Energy & Fuels, 20, 1906-1913 (2006). https://doi.org/10.1021/ef060060b

Palmer, J. C., Moore, J. D., Roussel, T. J., Brennan, J. K., Gubbins, K. E. Adsorptive behavior of CO_2, CH_4 and their mixtures in carbon nanospace: a molecular simulation study. Physical Chemistry Chemical Physics, 13, 3985-3996 (2011). https://doi.org/10.1039/c0cp02281k

Pawar, R. R., Patel, H. A., Sethia, G., Bajaj, H. C. Selective adsorption of carbon dioxide over nitrogen on calcined synthetic hectorites with tailor-made porosity. Applied Clay Science, 46, 109-113 (2009). https://doi.org/10.1016/j.clay.2009.07.009

Peng, X., Wang, W., Xue, R., Shen, Z. Adsorption separation of CH_4/CO_2 on mesocarbon microbeads: experiment and modeling. AIChE Journal, 52, 994-1003 (2006). https://doi.org/10.1002/aic.10723

Przepiórski, J., Skrodzewicz, M., Morawski, A. W. High temperature ammonia treatment of activated carbon for enhancement of CO_2 adsorption. Applied Surface Science, 225, 235-242 (2004). https://doi.org/10.1016/j.apsusc.2003.10.006

Purna Chandra Rao, G., Satyaveni, S., Ramesh, A., Seshaiah, K., Murthy, K. S. N., Choudary, N. V. Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite. Journal of Environmental Management, 81, 265-272 (2006). https://doi.org/10.1016/j.jenvman.2005.11.003

Shen, Y., Bai, J. A new kind CO_2/CH_4 separation material: open ended nitrogen doped carbon nanotubes formed by direct pyrolysis of metal organic frameworks. Chemical Communications, 46, 1308-1310 (2010). https://doi.org/10.1039/b913820j

Su, F., Lu, C., Chen, H.-S. Adsorption, desorption, and thermodynamic studies of CO_2 with high-amine-

loaded multiwalled carbon nanotubes. Langmuir, 27, 8090-8098 (2011). https://doi.org/10.1021/la201745y

Su, F., Lu, C., Cnen, W., Bai, H., Hwang, J. F. Capture of CO_2 from flue gas via multiwalled carbon nanotubes. Science of The Total Environment, 407, 3017-3023 (2009). https://doi.org/10.1016/j.scitotenv.2009.01.007

Su, F., Lu, C., Kuo, S.-C., Zeng, W. Adsorption of CO_2 on amine-functionalized Y-type zeolites. Energy & Fuels, 24, 1441-1448 (2010). https://doi.org/10.1021/ef901077k

Wang, S., Lu, L., Lu, X., Cao, W., Zhu, Y. Adsorption of binary CO_2/CH_4 mixtures using carbon nanotubes: Effects of confinement and surface functionalization. Separation Science and Technology, 51, 1079-1092 (2016). https://doi.org/10.1080/01496395.2016.1150296

Xiang, Z., Cao, D., Lan, J., Wang, W., Broom, D. P. Multiscale simulation and modelling of adsorptive processes for energy gas storage and carbon dioxide capture in porous coordination frameworks. Energy & Environmental Science, 3, 1469-1487 (2010). https://doi.org/10.1039/c0ee00049c

Zhang, C., Liu, Q., Xu, Z. Synthesis and characterization of non-crystalline mesoporous silicon oxynitride MCM-41 with high nitrogen content. Journal of Non-Crystalline Solids, 351, 1377-1382 (2005). https://doi.org/10.1016/j.jnoncrysol.2005.03.035

Zhou, Z., Anderson, C. M., Butler, S. K., Thompson, S. K., Whitty, K. J., Shen, T.-C., Stowers, K. J. Stability and efficiency of CO_2 capture using linear amine polymer modified carbon nanotubes. Journal of Materials Chemistry A, 5, 10486-10494 (2017). https://doi.org/10.1039/C7TA02576A